Nanotubes in a New Light

Using x-rays to investigate order and function in nanotube systems

Nanotubes are cylindrical molecules just a few nanometers (billionths of a meter) in diameter. However, their potential for new technologies is vast. They are extraordinarily strong, conduct electricity well, and can even emit light, properties suitable for many applications, from flat-panel television displays to building materials. But nanotubes must be extensively studied before they can be used in industrial applications.

A collaboration of scientists has pioneered a novel way of using x-rays to study arrays of nanotubes. In ongoing research, they have determined the degree of order contained in certain nanotube systems — that is, to what extent they form organized patterns — and have investigated the structural and chemical properties of others.

The team includes Mahalingam Balasubramanian, Brookhaven National Laboratory (BNL); Sarbajit Banerjee, Stony Brook University (SBU); Tirandai Hemraj-Benny, SBU; Daniel Fischer, National Institute of Standards and Technology (NIST); Weiqiang Han, BNL; James Misewich, BNL; Sharadha Sambasivan, NIST; and Stanislaus Wong, BNL and SBU.

The group is investigating two types of carbon nanotubes: single-walled nanotubes (SWNTs), consisting of a single cylinder, and multi-walled nanotubes (MWNTs), which resemble cylinders concentrically nested together. They have also completed a study of boron nitride nanotubes, which are equally intriguing.

A New Approach

Nanotubes are being studied across the globe, and the technique used in this case has been used for years to study various materials. Now, the technique has been applied to nanotubes, with excellent results.

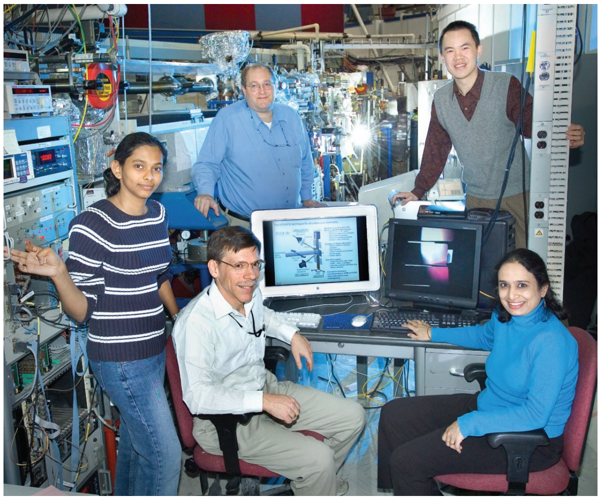
The technique is called “near-edge x-ray absorption fine structure,” or NEXAFS. In NEXAFS analysis, a nanotube sample is bombarded by a beam of low-energy x-ray “photons,” or particles of light. The photons are absorbed by each carbon atom’s “core” electrons — those closest to the nucleus - giving them an energy boost. As a result, they jump to an orbit further away from the nucleus. When this occurs across many, many atoms, scientists can record the sample’s absorption “spectrum,” which measures its absorption behavior.

At beamline U7A (owned by NIST and The Dow Chemical Company), the researchers aimed the x-rays at each sample from several angles, producing several spectra for each array. By analyzing the spectra, they uncovered information about the nanotubes’ electronic and physical structures.

“The beauty of using NEXAFS to study nanotubes is that it is able to provide us with detailed information that is truly complementary to what can be obtained using other techniques,” said Fischer.

Your Order, Please

In the May 5, 2005 issue of the *Journal of Physical Chemistry*, the group describes how they used NEXAFS to determine the degree of order in very thin films of single-walled nanotubes, known as “buckypaper,” and a MWNT film grown on a surface of platinum. They compared their results to two “control” groups: graphite, a highly ordered form of carbon, and SWNT and MWNT powders, which have essentially no order.

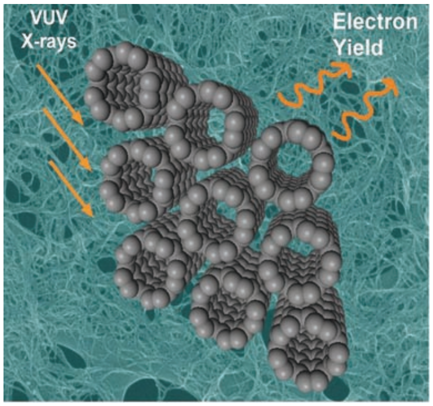


Authors (from left) Tirandai Hemraj-Benny, Dan Fischer, Jim Misewich, Stanislaus Wong, and Sharadha Sambasivan

The group found that the buckypaper spectra are similar to graphite’s. For both, the spectra change when the x-rays graze the sample rather than strike head-on. This property — the tendency of a material to react differently to outside fields depending on the direction the field is applied — is called “anisotropy.” It is very useful to study, since high anisotropy often implies a high degree of order. Conversely, a material shows “isotropy” when its reaction to an outside field is the always the same. Nanotube powders, containing nanotubes in all possible orientations, display isotropy.

The buckypaper displayed anisotropy, but not as extensively as graphite — approximately 87 percent of the nanotubes were on their sides. The MWNT film was also quite anisotropic, behaving as if most of the nanotubes were standing upright.

“These results are encouraging because they indicate that two common nanotube systems already contain a fair degree of order," said Wong. "We plan to continue studying MWNT and SWNT films. Our hope is to find a way to produce a nanotube array with order comparable to graphite."



A rendering of carbon nanotubes being studied using NEXAFS. Light comes in (left) and electrons are emitted (right).

A Matter of Function

"Functionalizing" a set of nanotubes is a process that allows scientists to manipulate the tubes into ordered arrays with specific properties. One way to do this is "ozonolysis" — reacting the nanotubes with ozone, a form of oxygen gas. This produces tiny holes into the nanotubes' walls and creates various oxygenated compounds along their surfaces, which serve as tethering points for a variety of other compounds.

Ozonolysis can also cleanse the nanotubes or produce reactions that "unhinge" the nanotubes' half-sphere end caps, leaving the tubes open to a variety of interesting "stuffings." Filling the tubes with metal atoms, for example, could boost their ability to conduct electricity.

But studying the specific electronic structure of the nanotubes, as well as the chemical make-up and ordering of the oxygen-carbon compounds, which are called functional groups, has been difficult. Most techniques are unable to simultaneously yield both types of information. The team showed that NEXAFS is an important complement to these other methods.

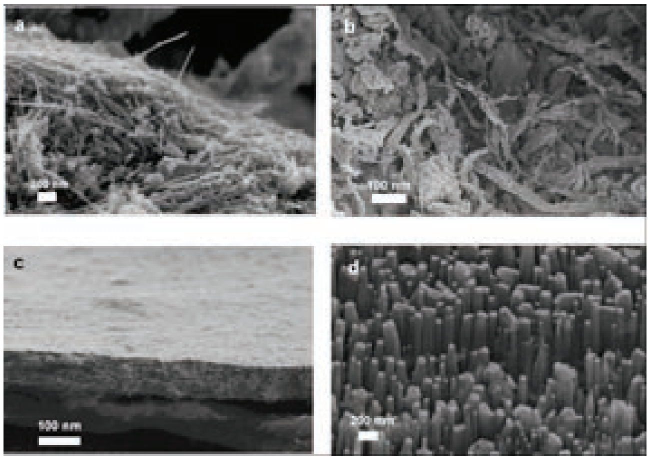
For example, their article in the September 20, 2004 issue of *ChemPhysChem*, focuses on MWNTs exposed to ozone. NEXAFS showed that the ozone treatment cleared the nanotubes of "amorphous" carbon — carbon atoms not incorporated into the ordered structure of the nanotubes themselves — opened the end caps, and produced functional groups along the nanotubes.

A Nanotube by Another Name

The word "nanotube" is very often preceded by the word "carbon," but nanotubes made of other materials can be equally — or even more — interesting. One such material is boron nitride.

Boron nitride nanotubes are also tremendously strong. But they possess some superior properties, such as flexibility without compromising strength and the ability to withstand very high temperatures. Like carbon nanotubes, they are being investigated for a wide array of potential applications.

In the March 21, 2005 issue of the journal *Physical Chemistry Chemical Physics*, the team describes how they used NEXAFS to gain valuable structural information about a sample of boron nitride nanotubes. Their results show that the nanotubes in their sample have atomic structures that mimic a type of carbon nanotube with hexagonally bonded carbon atoms (like a rolled-up sheet of chicken-wire fence). NEXAFS also revealed that the boron nitride nanotubes have few defects and are highly crystalline, perhaps even more so than carbon nanotubes.



Scanning electron microscope images of (a) MWNT powder, (b) SWNT powder, (c) SWNT buckypaper, and (d) aligned MWNTs.

For more information, see:

S. Banerjee, T. Hemraj-Benny, S. Sambasivan, D.A. Fischer, J.A. Misewich, and S.S. Wong, "Near-Edge X-ray Absorption Fine Structure Investigations of Order in Carbon Nanotube-Based Systems," J. Phys. Chem. B, ***109(17)****, 8489-8495 (2005).*

S. Banerjee, T. Hemraj-Benny, M. Balasubramanian, D.A. Fischer, J.A. Misewich, and S.S. Wong, "Surface Chemistry and Structure of Purified, Ozonized, Multiwalled Carbon Nanotubes Probed by NEXAFS and Vibrational Spectroscopies," ChemPhysChem., ***5(9)****, 1416-1422, (2004).*

T. Hemraj-Benny, S. Banerjee, S. Sambasivan, D.A. Fischer, W. Han, J.A. Misewich, and S.S. Wong, "Investigating the Structure of Boron Nitride Nanotubes by Near-Edge X-ray Absorption Fine Structure (NEXAFS) Spectroscopy," Phys. Chem. Chem. Phys., ***7(6)****, 1103-1106 (2005).*

— Laura Mgrdichian